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**13. ABSTRACT**   A method of tuning and analyzing the fracture properties of polymer/nonpolymer interfaces by the controlled addition to the interface of deuterium labelled block copolymers has been developed. Forward recoil spectrometry (FRES) was used to measure the interface excess of the labelled copolymers and this technique along with Rutherford backscattering spectrometry was used to determine the locus of fracture along the interface, thus revealing molecular details of the fracture process.  These results were correlated with the fracture toughness $G_c$ measured using an asymmetric cantilever beam specimen developed to guide the crack along the interface of interest. A model system consisting of an interface between glass and polystyrene with block copolymers of deuterated polystyrene (d-PS) and poly(2vinylpyridine) (PVP) was used.  Effective methods for manipulating the $G_c$ were discovered, even at a modest areal chain density of the block copolymer, by changing the lengths of the d-PS and PVP blocks thus avoiding pull-out of the dPS block from the PS and pull-off of the PVP from the glass.  Forming a self-assembled methyl-terminated monolayer on the glass led to very low $G_c$ by preventing hydrogen bonding between the PVP and  silanol groups on the glass.

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# Tailored Polymer Nonpolymer Interfaces for Controlled Adhesion

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10/14/95

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Final Report

to

Army Research Office

E. J. Kramer

The control of cracking along interfaces between a rigid polymer and either another polymer or a non-polymeric material is of interest in a number of critical applications. For example in electronic packaging, polymeric dielectric layers between metals and semiconductors are being used increasingly because of their low dielectric constant. Such packages may eventually consist of many alternating layers. Failure of the interfaces (polymer-polymer, polymer-metal, polymer-semiconductor) is invariably deleterious to the electrical and thermal performance of the package and must be avoided despite imposed stresses due to temperature and humidity cycling.

In his work under this grant, Kramer and coworkers have shown that they can dope homopolymer layers with small amounts of either block copolymers or end functionalized chains, which segregate, and bond strongly to certain polymer/oxide coated Si interfaces as well as to certain interfaces between this homopolymer and a second, immiscible homopolymer. The amount of such segregation was measured using forward recoil spectrometry and controlled by changing the initial concentration of segregating polymer in the homopolymer layer. They have also discovered that this segregation increases the adhesion of this layer to the substrate. During this grant Kramer has concentrated on 1.) quantifying the relationship between the amount of segregated polymer component at the interface and the final volume fraction $\varphi_\infty$ of segregating polymer in the homopolymer layer well away from the interface

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and 2.) on showing how that knowledge of that segregation isotherm could be used to tailor the interface fracture energy $G_c$.

Segregation Studies:

The amount of segregated polymer was determined as the interface excess $z^*$ defined as

$$z^* = \int \left( \varphi(z) - \varphi_\infty \right) dz \qquad (1)$$

where z is the distance normal to the interface and $\varphi(z)$ is the volume fraction at that distance. The integral excess is likely to be the most important quantity controlling the fracture properties of the modified interface, since $\Sigma$, the number of segregating chains per unit area at the interface, is directly proportional to it, as given by the following relationship:

$$\Sigma = z^* \rho_o \, / \, N_c \qquad (2)$$

where $\rho_O$ is the polymer segment density of the block copolymer and $N_c$ is the degree of polymerization of that segregating polymer.

One set of experiments measured the segregation of a diblock copolymer of deuterated polystyrene (d-PS) and poly2vinylpyridine (PVP) to silicon covered with its native oxide. Several different block copolymers of deuterated polystyrene and poly(2-vinyl pyridine) (dPS-PVP) were synthesized by anionic polymerization. their degrees of polymerization and polydispersity indices were determined with gel permeation chromatography (GPC), forward recoil

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spectrometry (FRES), and $^{13}$C nuclear magnetic resonance (NMR) and are shown in Table 1.

Table I

| $N_{dPS}-N_{PVP}$* | $N_c$† | PDI |
|---|---|---|
| 520-22 | 542 | 1.08 |
| 656-46 | 702 | 1.02 |
| 284-67 | 351 | 1.08 |
| 391-68 | 459 | 1.03 |

* Degrees of polymerization of the dPS and PVP block of the copolymer respectively

† $N_c$ is the total degreee of polymerization of the block copolymer chain.

Blends of each dPS-PVP block copolymer and a 670,000 molecular weight PS homopolymer (degree of polymerization P$_{PS}$=6440) were made into 5 weight percent solutions in toluene, with concentrations of dPS-PVP below the critical micelle concentration. Using a Headway resist spinner, these solutions produced films 4500 Å thick when spun at 2000 rpm until dry. The samples were annealed between 8 and 10 hours at 178°C in a vacuum oven at $10^{-2}$ Torr. From previous experiments on the same dPS-PVP diblock copolymers at interfaces between PS and PVP homopolymers, this length of time was sufficient for the system to reach equilibrium.

The experimental technique of FRES was used to measure the segregation. An alpha particle beam with incident energy 2.7 MeV causes $^{1}$H and $^{2}$H nuclei to recoil out of the sample. The energy of recoiling $^{1}$H and $^{2}$H nuclei from deeper

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below the surface decreased because energy losses for incident alpha particles and recoiled hydrogen and deuterium ions are greater from deeper within the samples. Concentration versus depth profiles for deuterium (and thus the dPS-PVP copolymer) were determined to depths of up to 5000 Å without overlap with the hydrogen signal. The resolution of this technique is $\approx$ 80nm.

Figure 1 shows a typical depth profile of a dPS-PVP copolymer in the PS homopolymer on a silicon wafer with its native oxide layer. The dPS-PVP copolymer had degrees of polymerization of 381 for the dPS block and 68 for the PVP block. In the following, the notation $N_{dPS}$-$N_{PVP}$, or in this case 381-68, to describe each block copolymer, will be used.

Strong segregation of the dPS-PVP block copolymer to the interface between the silicon oxide and the polymer melt was observed . Figure 2(a)-(d) show the segregation isotherms obtained for the different dPS-PVP copolymers. The interface excess $z^*$ is plotted against $\varphi_\infty$, the bulk dPS-PVP concentration. The solid lines are guides to the eye. The rapid rise in $z^*$, followed by a level plateau, is characteristic for all the segregation isotherms of dPS-PVP to the SiOx interface. The segregation is observed to be very strong, leading to saturation below $\varphi_\infty$=0.02 for all the copolymers in Table 1. The strong segregation presents some problems for analyzing the data. Due to the rapid rise of $z^*$ at extremely low $\varphi_\infty$ for the segregation, even small errors in measuring the (very small) deuterium signal in the bulk phase result in large errors in the initial low concentration slope of the isotherms.
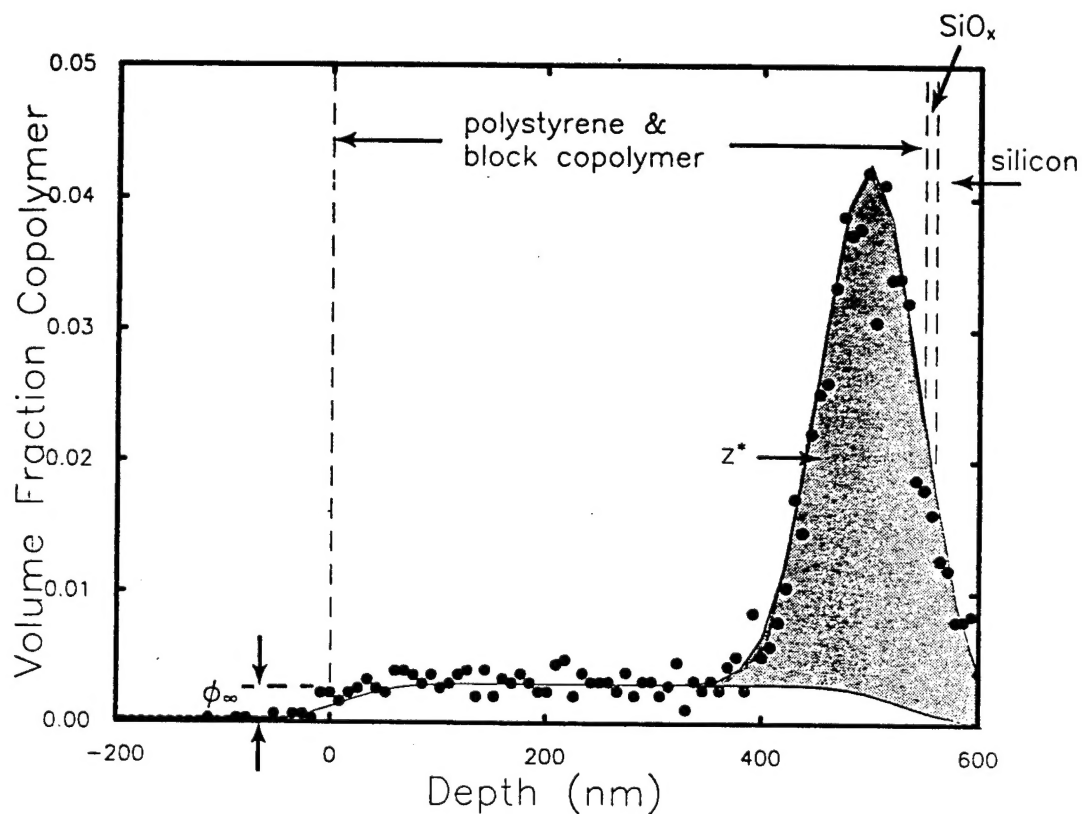
Figure 1: Depth profile of dPS-PVP with degrees of polymerization $N_{dPS}$-$N_{PVP}$=381-68 in a layer of 670k PS homopolymer. The locations of the substrate silicon oxide and silicon are shown schematically. The shaded area is the integral interfacial excess z*. The bulk concentration of block copolymer, $\varphi_{\infty}$, is also indicated in the diagram.
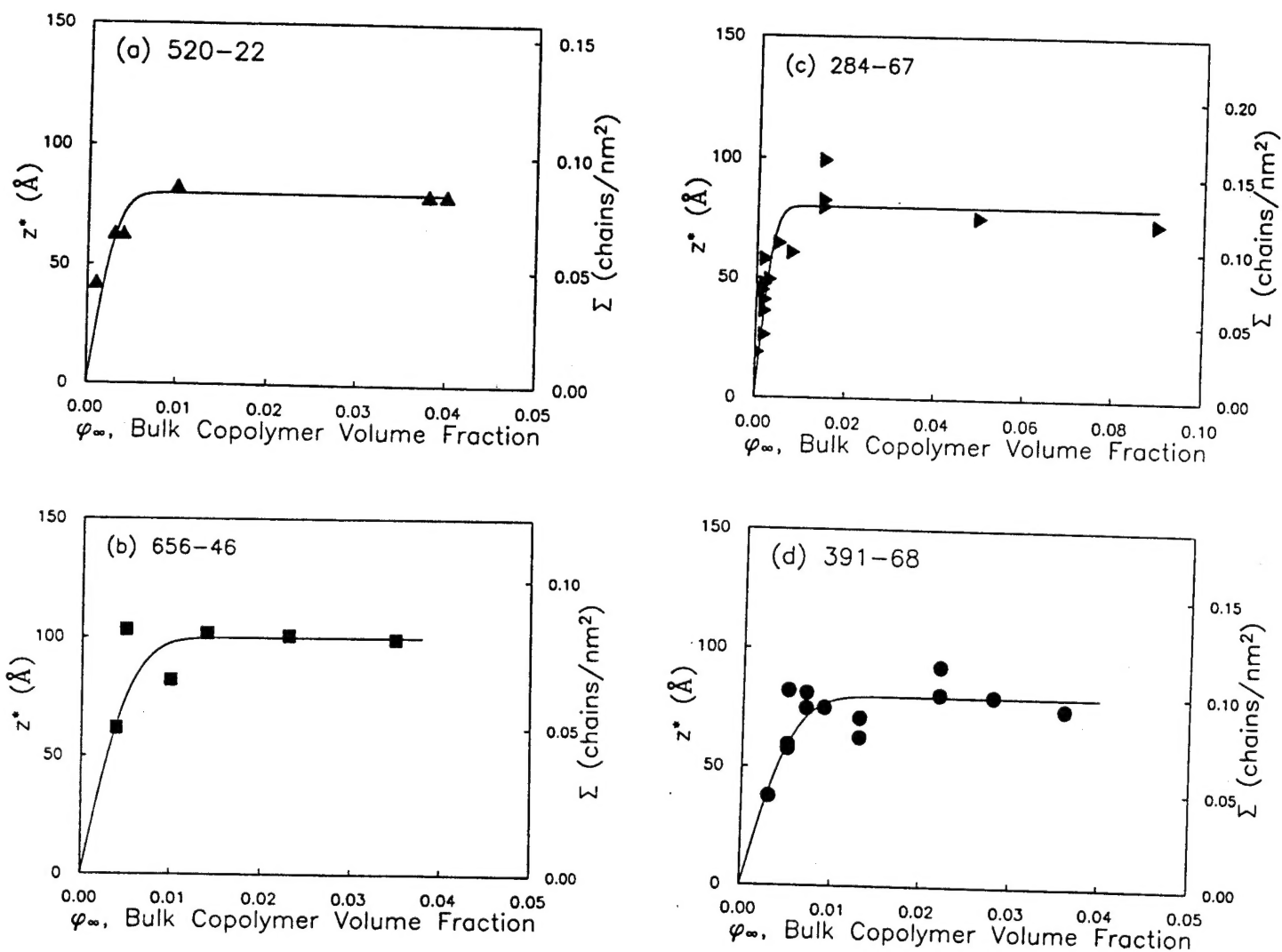
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Figure 2: z* versus φ∞ for segregation of dPS-PVP block copolymer chains to the interface of PS-SiOx. The solid lines are guides to the eye. (a) Data for 520-22 dPS-PVP. (b) Data for 656-46 dPS-PVP. (c) Data for 284-67 dPS-PVP. (d) Data for 391-68 dPS-PVP. The solid lines are guides to the eye.

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Enthalpic forces from the repulsive interaction between the PVP and the PS and the attractive interaction between the PVP and the oxide drive the PVP to the interface. The repulsive interactions in the bulk may be accounted for by the Flory interaction parameter between PS and PVP: $\chi_{PS\text{-}PVP} \approx 0.106$ at the annealing temperature. At the same time, entropic forces resist the tendency for the dPS ends of the block copolymer to stretch into the PS homopolymer. These data were used to determine the attractive interaction between the PVP and the oxide using an analysis based on the self-consistent mean field theory results of Shull [K.R. Shull, J. Chem. Phys **94** 5723 (1991)].

Shull's expression for the chemical potential of the block copolymer in the bulk can be simplified with the following conditions which are well satisfied in our experiments:

(1) the copolymer concentration in bulk, $\varphi_\infty \ll 1$;

(2) the concentration of PVP in the bulk PS, $\varphi_{PVP} \ll 1$; and

(3) the concentration of PS in the bulk, $\varphi_{PS} \approx 1$. Then the chemical potential of the dPS-PVP block copolymer in the bulk becomes

$$\frac{\mu}{k_B T} = \ln(\varphi_\infty) + 1 - \frac{N_c}{P_{PS}} + \chi_{PS-PVP} N_{PVP} \quad (3)$$

where $N_c$, $N_{PVP}$, $P_{PS}$ are the degrees of polymerization of the dPS-PVP copolymer, the PVP part of the copolymer, and the PS homopolymer, respectively, and $\chi_{PS\text{-}PVP}$ is the Flory interaction parameter between PS and PVP. Shull's expression for the chemical potential of a end-functinalized polymer at the interface can be modified to approxiamte that of an asymmetric block copolymer at the interface:

$$\frac{\mu}{k_B T} = \frac{\Phi_{eff}}{k_B T} - 1.1 \ln\left(\frac{\delta}{R_g^{dPS}}\right) + \frac{\bar{\mu}}{k_B T} \qquad (4)$$

where $\Phi_{eff}$ is the effective potential with which the PVP block of the copolymer and the surface interact, $\delta$ is the range over which the interaction between the surface and the block copolymer takes place, $R_g^{dPS}$ is the radius of gyration of the dPS block of the copolymer, and $\bar{\mu}$ is the stretching chemical potential. In what follows, the numerical results of Shull for the dependence of $\frac{\bar{\mu}}{k_B T}$ on $\frac{z^*}{R_g}$ were used. Following Shull, $\delta$ is set equal to the statistical segment length a so that $\frac{\delta}{R_g^{dPS}}$. Since $\Phi_{eff}$ is the potential represnting the interaction between the PVP block copolymer copolymer and the silicon oxide surface, it shoud depend on $N_{PVP}$ and an interaction parameter $\chi$ between the PVP segmenst and the oxide. In the limit where there are many more PVP bonding sites on the surface than PVP segments, $\Phi_{eff} \approx N_{PVP} \chi$. In general, however, not all $N_{PVP}$ segments will be able to bond to the surface, i.e. only a fraction f of such segments will bond. For a particular areal density of copolymer chains at the interface, $\Sigma$, we expect that f will decrease as $N_{PVP}$ increases.

At equilibrium in the segregation experiments the chemical potential of the block copolymer must be the same at the interface and in the bulk and thus $\mu$ from Eq. 3 can be set equal to $\mu$ from Eq. 4, resulting in the following expression for the stretching part of the chemical potential:

$$\frac{\overline{\mu}}{k_B T} = \ln(\varphi_\infty) + 1 - \frac{N_c}{P_{PS}} + \chi_{PS-PVP} N_{PVP}$$
$$+0.55 \ln\left(\frac{6}{N_{dPS}}\right) - \frac{\Phi_{eff}}{k_B T} \qquad (5)$$

All the terms of Eq.5 are known except for the stretching chemical potential and the effective potential between the PVP block and the silicon oxide. Figure 3 shows the normalized interface excess, $z^*/R_g{}^{dPS}$, as a function of the stretching chemical potential plus the effective potential between the PVP block and the oxide. Each set of data is roughly linear and offset from the solid line, which represents the universal curve of Shull with $\Phi_{eff}=0$. The experimental data systematically deviate from the universal curve, due to the potential $\Phi_{eff}/k_B T$, which is dependent on the degree of polymerization of the PVP block of the copolymer and the effective interaction between the PVP and the silicon oxide. The dashed lines through each data set are used determine $\Phi_{eff}/k_B T$ for each set of data.

Figure 4 is a plot of $\Phi_{eff}/k_B T$ versus $N_{PVP}$, with $\Phi_{eff}/k_B T$ derived from the intercepts of the dashed lines of Figure 3.4. The solid line is a linear fit of the points. The effective potential $\Phi_{eff}/k_B T$ is large and negative, corresponding to a strong attractive interaction between the PVP block and the silicon oxide. It is extremely surprising that the magnitude of the attractive potential $\Phi_{eff}/k_B T$ actually decreases as $N_{PVP}$ increases. This result indicates that not just a smaller fraction of PVP segments can interact with the SiOx surface as $N_{PVP}$ increases, but actually a smaller absolute number.
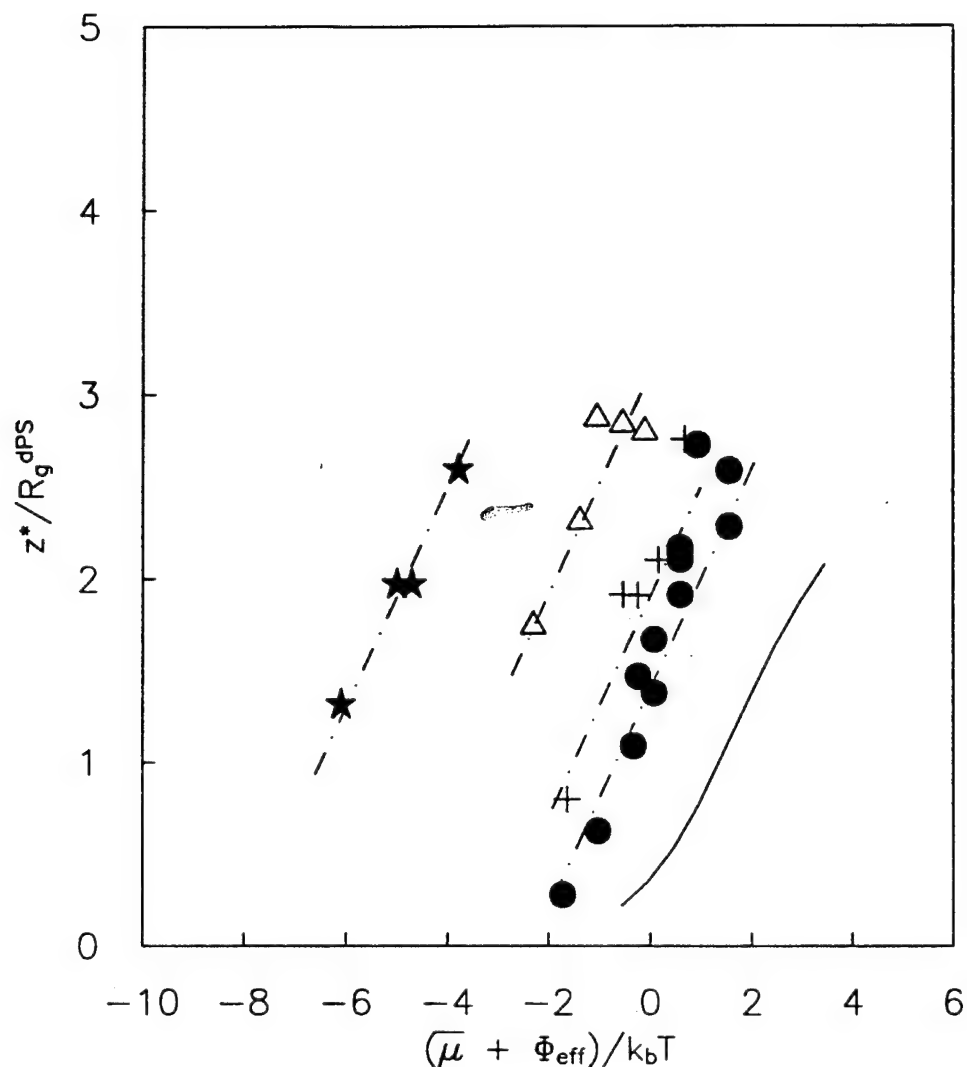
Figure 3: Normalized interfacial excess, z*/Rg, versus $\dfrac{\overline{\mu} + \Phi_{eff}}{k_B T}$.

Only segregation data with z* values below the saturation of the interface are shown. The solid line is the universal curve calculated from self-consistent mean field theory with $\Phi_{eff}=0$. The dashed lines are the linear fits through data for each block copolymer. ★ are 520-22 dPS-PVP; Δ are 656-46 dPS-PVP; + are 284-67 dPS-PVP; and ● are 381-68 dPS-PVP.
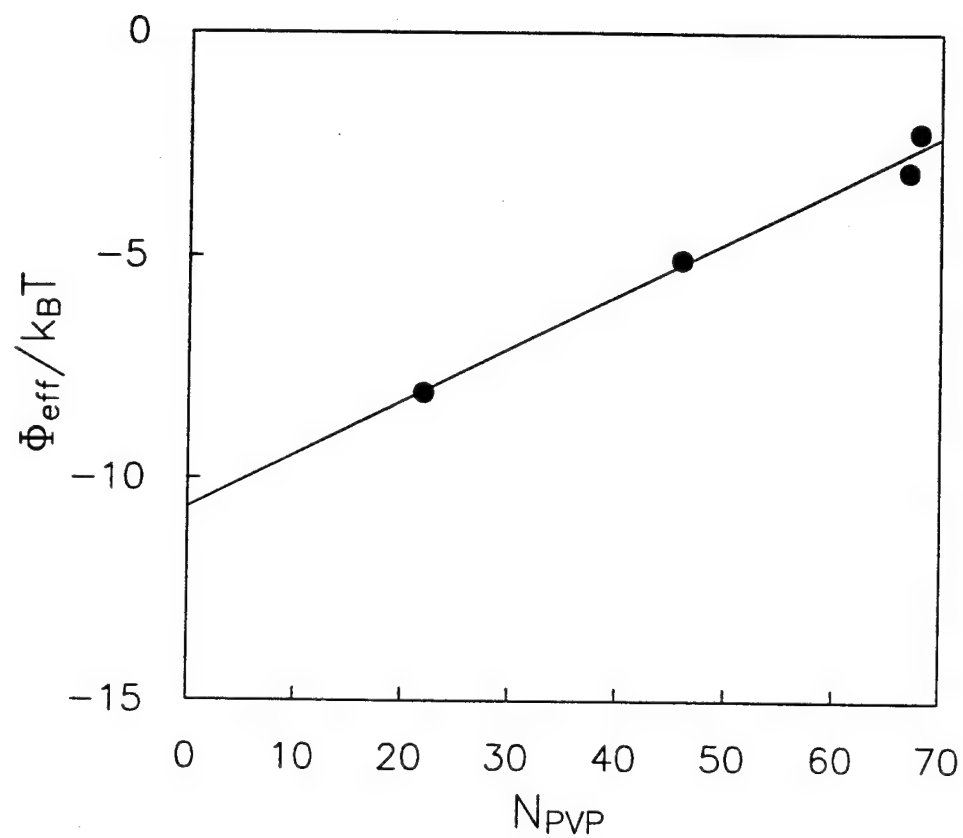
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Figure 4: $\Phi_{eff}/k_BT$, the effective interaction between the PVP block and the silicon oxide interface, versus $N_{PVP}$. The solid line is a linear fit.

The results shown in Figure 4 are internally consistent but nonetheless very surprising. The magnitude of $\Phi_{eff}/k_BT$ actually decreases with increasing $N_{PVP}$. Longer PVP blocks actually apparently experience a weaker (though still strong) attraction to the oxide than shorter ones. One possibility is that the Flory-Huggins mean field theory used to compute the chemical potential of the copolymer in the bulk is in error. While this possibility exists (The PVP coil might collapse producing an interaction with the PS homopolymer that would scale not as $N_{PVP}$ but as $(N_{PVP})^{2/3}$.), no hint of such problems were observed when the segregation of the same block copolymers was measured at PS/PVP interfaces [ Dai and Kramer, J. Polymer Sci.-Polymer Phys., **32** 1943 (1994).] The most likely explanation is that due to a very strong interaction between PVP and the silanol groups on the oxide surface, that the initial adsorption of a long PVP block on the oxide surface, effectively block the adsorption of subsequent PVP blocks. In any case our segregation results show that short PVP blocks can be very effective in driving the block copolymer to the oxide-polystyrene interface, a conclusion that is reinforced by the studies of adhesion reported in the next section

### Tailoring Interfacial Fracture Properties

### Fracture Testing Methods and Specimen Preparation

:   Common tests for measuring polymer-nonpolymer adhesion are riddled with problems which are intrinsic to the types of materials being measured and are thus difficult to circumvent. Engineering tests such as the peel and blister tests are often more sensitive to the nonelastic deformation occurring far from the crack tip in the polymer than to the actual adhesion. Tests using standard fracture mechanics

specimen such as the single edge notch specimen are often limited in the applicability as such specimens often fail by cracking of the polymer away from the interface, are expensive to produce and result in only one measurement per specimen making attempts to generate statistically significant data very difficult. More fundamental approaches, such as the measurement of forces between surfaces in near contact might be expected to provide a wealth of information about the molecular affinity between the polymer and the nonpolymer but are normally unable to reproduce the local crack tip deformation mechanisms near the interface, such as crazing, which can have significant effects on the magnitude of the interfacial fracture energy Gc. In light of the importance of these localized deformation mechanisms, a fracture mechanics approach, modified to eliminate some of the difficulties noted above, is the most useful approach to the problem.

Over the course of this grant Kramer and his collaborators have developed a double cantilever beam fracture specimen which has these characteristics and have used it to make fracture toughness measurements on interfaces between polystyrene (PS) and glass that have been strengthened by the addition of deuterated polystyrene - poly(2vinylpyridine) (dPS-PVP) block copolymers. The PVP hydrogen bonds to the silanol groups on the glass and the dPS block, if long enough, will entangle with the PS homopolymer. The exploded view of Figure 5 shows the structure of the double cantilever beam specimen. Glass slabs, of unequal thickness, form the two beams. A thin layer (~ 2 to 10 nm) of the block copolymer is spun onto the thinner beam from solution. A much thicker (~4 µm) PS film is spun onto a glass plate, floated off onto water, and then transferred onto the copolymer coated glass slab. These coated slabs were then annealed for three hours at 160°C in vacuum to produce an equilibrium interface.
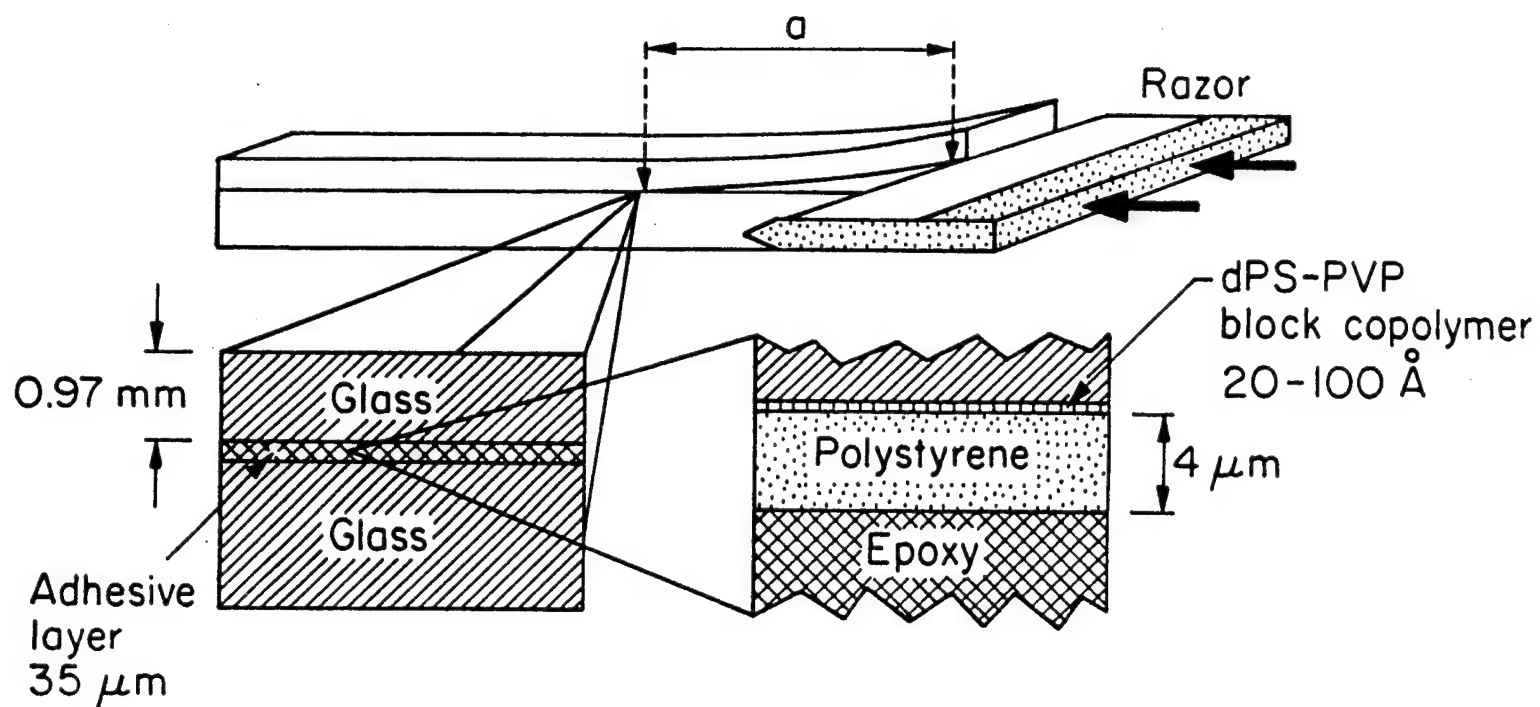
Figure 5. Schematic of the asymmetric double cantilever beam specimen.

The top surface of the PS layer is bonded to the thicker glass slab using a thin layer of an epoxy resin, after first oxygen plasma etching the polystyrene surface to produce suitable polar surface groups which can react with the epoxy. The glass/copolymer/PS/epoxy/glass sandwich is then annealed at 100°C for 2 hours to cure the epoxy. From each glass slab several 7.5 mm wide samples are cut using a water lubricated diamond saw. After polishing the edges of these samples to remove cracks in the glass, they were left in a vacuum desiccator overnight to remove moisture from the cutting and polishing procedure.

The test itself involves forcing a razor blade between the two beams causing the interface between the PS and the thinner glass beam to crack ahead of the blade. A small testing jig was constructed which drives the razor blade at a constant rate and the length of the crack ahead of the razor blade is measured at many points along the specimen using a television camera and VCR system. From each measurement of the crack length a we can compute one value of fracture energy $G_c$, allowing us to make many measurements on the same specimen and to determine the statistical spread of these measurement. After the fracture experiment has been terminated, forward recoil spectrometry was used both to measure $\Sigma$, the areal density of block copolymer at the interface, by determining the total amount of deuterium on both sides of the fracture surface and to locate the dPS block after fracture, i.e. what fraction of it was on the glass side of the fracture surface and what fraction was on the PS side. The PVP block was quaternized by reaction with methyl iodide and the relative amount of PVP on each side of the fracture surface was determined similarily by Rutherford backscattering spectrometry (RBS). The ion beam analysis shows very clearly what the mechanism of fracture of the interfaces reinforced with the two different block copolymers is.

The Mechanical Phase Angle:

In collaboration with Prof. C.-Y. Hui and his student F. Xiao, Kramer carried out a thorough analysis of the ADCB specimen using both a boundary element numerical method and a more approximate, analytical method originally due to Kanninen [ M.F. Kanninen, Int. J. of Fracture, **9** 83 (1973)] to determine the relationship between the strain energy release rate G and the geometry of the specimen to determine for all likely specimen geometries and elastic properties of the two beams. This this analysis was used to determine the complex stress intensity factor $K = K_1 + iK_2$ , where $i = (-1)^{1/2}$. Specifically, the traction directly ahead of the crack tip along the interface has both a shear ($\sigma_{xy}$) and a tensile ($\sigma_{yy}$) component. The ratio of the shear stress to the tensile stress directly ahead of the crack tip at x = d, where d is a distance that is small compared to typical specimen dimensions, is related to a phase angle $\Psi$ by:

$$(\sigma_{xy}/\sigma_{yy})_{x=d} = \tan \Psi = \text{Im}(Kd^{i\varepsilon})/\text{Re}(Kd^{i\varepsilon}) \tag{6}$$

where $\varepsilon$ is a dimensionless material parameter which depends on mismatch of elastic moduli between the two materials on either side of the interface. For the glass/PS/glass system $\varepsilon \approx 0$ due to the thinness of the PS layer, which means that our phase angle $\Psi$ depends negligibly on d. The energy release rate G, together with the phase angle $\Psi$, completely characterize the stress field near the crack tip.

Cracks, and any crazes preceding them, tend to propagate toward a direction which minimizes the local $\sigma_{xy}$ and thus $\Psi$. This tendency is especially pronounced for polymer/glass interfaces when the polymer has a lower Young's modulus than the glass and a low crazing stress as does PS.

At PS/glass interfaces in symmetrically loaded specimens ($h_1 = h_2$ where $h_1$ and $h_2$ are the thicknesses of the top and bottom glass beams) an interfacial crack and a craze would be driven toward the center of the thin PS layer due to the Young's

modulus mismatch and away from the treated interface, resulting in a larger $G_c$ compared with that of the interface itself. Such a phase angle is defined as positive.

In order to measure the true value of $G_c$, the testing geometry must therefore have a small negative phase angle $\Psi$, which compensates the modulus mismatch and forces an interfacial crack to propagate at the interface. The asymmetric double cantilever beam geometry (thicker glass top beam and thinner glass bottom beam which has the treated interface) used in this study satisfies this small negative $\Psi$ condition, ensuring that we will measure the $G_c$ of the interface itself. In addition the pahse angle $\Psi$ can be tuned by adjusting $h_1$ and $h_2$. However the specimen does introduce some difficulties. If the $G_c$ of the interface is large (i.e. when the adhesion at the interface is strong), a high enough tensile stress may be generated in the thinner glass beam just behind the crack tip to cause it to fracture; in the initial experiments this limited the maximum $G_c = G_{c,max}$ that could measured to less than ~ 25 J/m$^2$. As part of the study mentioned above, this problem was analysed in detail and it was shown that $G_{c,max}$ is given by

$$G_{c,max} = \sigma_f^2 h_2 B \tag{7}$$

where $\sigma_f$ is the fracture stress of the thin glass beam and B is a constant which depends only on the ratio $h_1/h_2$. Using Eq. 7 as a guide Kramer and collaborators scaled up the thicknesses of both beams (keeping $\psi$ constant but increasing $h_2$) and have polished the edges of the beams, thus increasing $\sigma_f$. With these improvements, they were able to routinely measure $G_c$'s of 100 J/m$^2$.

Interfacial Fracture Toughness:

For a long 800-870 block copolymer (The numbers in the block copolymer designation represents the polymerization index respectively of the dPS and PVP blocks) Kramer and coworkers find the dPS on the both sides of the fracture surface while all the PVP is on the glass side. Clearly the PVP has not been pulled off the

glass while the fact that some dPS is found on both sides of the fracture suggests that the dPS chain has undergone chain scission. A comparison between these results and Gc measurements of PS/PVP interfaces reinforced with the same block copolymer, where the fracture mechanism at low $\Sigma$ has been shown to be chain scission add support to this idea. At large areal chain densities the fracture toughness is so large that the one of the glass beams fractures.

In contrast, similar FRES and RBS measurements of the fracture surface of the glass-PS interface reinforced by a 125-43 dPS-PVP block copolymer provide convincing evidence that the short dPS block pulls out of the PS. While all the PVP is still found on the glass side of the interface, now all the dPS also is found on the glass side. The only way these results can be explained is if the dPS block pulls out of the PS before the dPS chains can be loaded to fracture. The increase in fracture toughness $G_c$ over the bare interface (no block copolymer) is relatively small.

The results for a 680-95 dPS-PVP block copolymer were particularly interesting. The 680-95 block copolymer is one with a relatively long dPS block (long enough to entangle well with the PS homopolymer) and a rather short PVP block which serves to anchor the block copolymer on the glass. Results for this block copolymer are shown in Figure 6. As shown in Fig. 6a, fracture energies of the order of 40 J/m$^2$ can be achieved at large $\Sigma$, values that are almost 2 orders of magnitude greater than the fracture energy of the bare interface. These values can only be obtained if a reasonably wide craze has formed on the PS side of the interface ahead of the crack as it propagates. In this regime however the results of the failure analysis, (Figs. 6b and 6c) show that all of the the dPS and PVP are on the PS side of the fracture, a result that must mean that the craze fails by pull-off of the PVP from the glass.
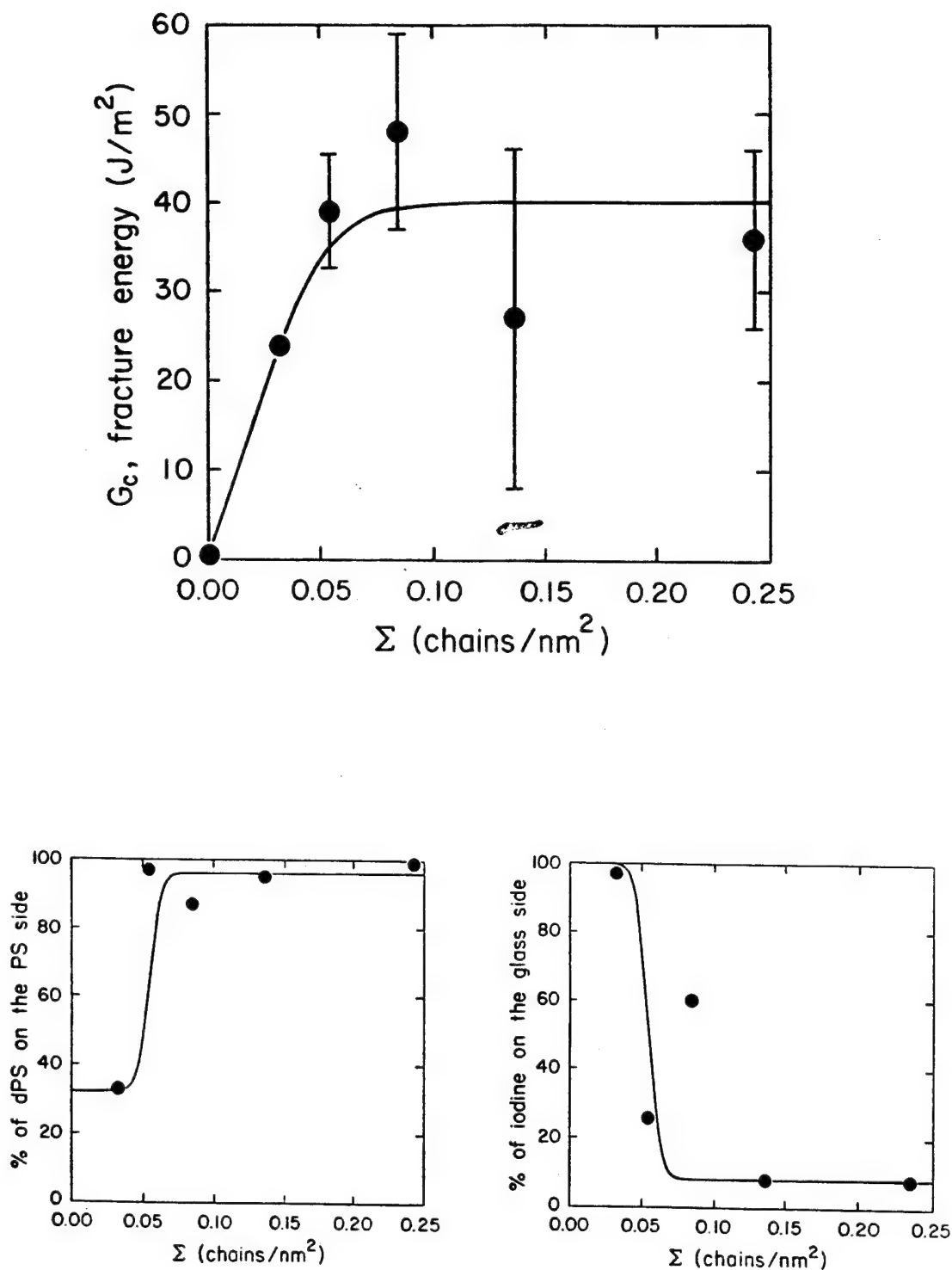
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Figure 6: a.) Interfacial fracture energy of glass-PS interfaces modified by a 680-95 dPS-PVP block copolymer. b.) and c.) percentage of dPS on the PS and PVP on the glass sides of the fracture surface, respectively.

At smaller values of $\Sigma$, (the point at 0.033 chains/nm$^2$), nearly all the PVP is on the glass as well as 70% of the dPS. While the large fracture energy (25 J/m$^2$) indicates that a craze is still formed, it must break down ahead of the crack tip primarily by breaking block copolymer chains. A model the pull-off failure has been developed to allow Kramer and coworkers to account for these results in terms of the force $f_g$ required to pull a single PVP segment off the glass and the area occupied by each PVP segment. We have used this model to develop a failure mechanism diagram for the PS/glass interface which is in qualitative agreement with the experimental results.

Extensive experiments were conducted with PS/glass interfaces modified by a 656-46 dPS-PVP block copolymer. The $G_c$ versus $\Sigma$ results shown in Fig. 7a show a transition in failure mechanism from chain scission (before crazing) at low $\Sigma < \Sigma^* = 0.03$ chains/nm$^2$ to crazing at higher $\Sigma$. The areal chain density at the transition is in excellent agreement with that observed for dPS chains grafted to PS/epoxy interfaces and for long dPS-PVP diblock copolymers at PS/PVP interfaces and corresponds to a force to break the dPS chain of ~ 2x10$^{-9}$ N. But in the larger areal chain density regime, it is apparent in Fig. 7b and c that nearly all the dPS is on the PS side of the interface but that all the iodine (and thus all the PVP) is on the glass side of the interface. The only conclusion possible is that the craze fails by breaking the dPS part of the diblock copolymer chain rather than pulling off the short PVP block from the glass surface. But such a result is in apparent contradiction with the results for the 680-95 dPS-PVP diblock for which the craze failed by pull-off of a longer PVP block. This paradox (That longer PVP blocks are less strongly anchored to the glass) can be resolved using the segregation data shown in Fig. 4. The attractive potential of the longer PVP block to the glass determined is indeed smaller than that of the shorter PVP block. These results demonstrate that rather subtle effects need to be

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taken into account in the design of block copolymers for strengthening polymer/nonpolymer interfaces.
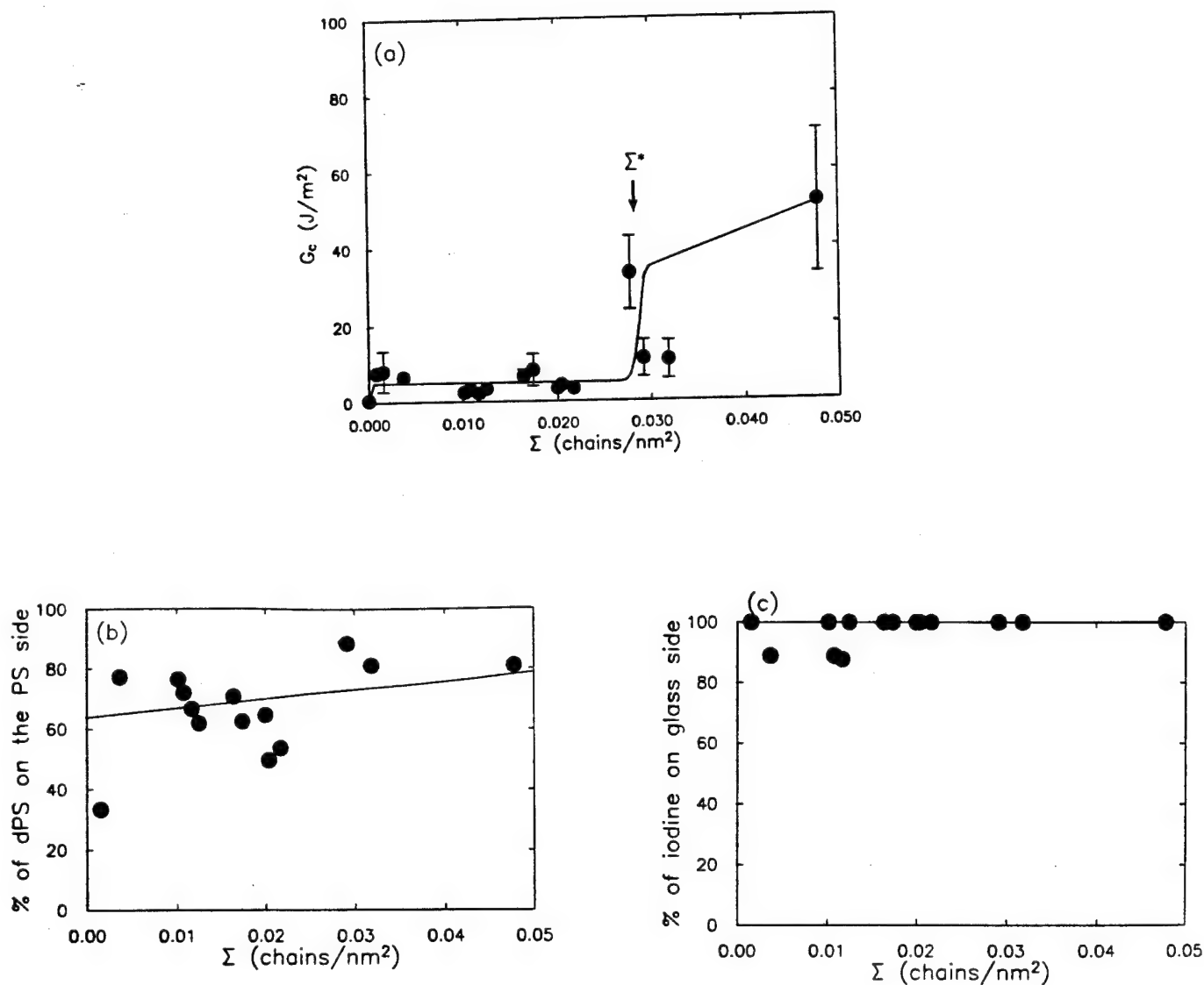


Figure 7. a.) Interfacial fracture energy of glass-PS interfaces modified by a 656-46 dPS-PVP block copolymer. b.) and c.) percentage of dPS on the PS and PVP (iodine) on the glass sides of the fracture surface, respectively.

A zwitterion-terminated dPS (which had a long dPS chain whose polymerization index N = 3125 and the zwitterion $[-N^+(CH_3)_2-(CH_2)_3-SO_3^-]$. at it end) had much less effect on the fracture toughness than the block copolymers, even though it segregated very strongly to the glass-PS interface. Even at an areal density $\Sigma = 0.1$ chains/nm$^2$ the fracture toughness of the interface has only increased from 0.5 for the bare interface to 2.5 J/m$^2$. In this case most of the dPS was found on the PS side of the fracture, suggesting that most of the zwitterions were ripped off the glass during the fracture process. Apparently the ionic attraction is not strong enough to lead to much reinforcement of the interface.

Finally self-assembled paraffin-like monolayers (SAM) formed by reacting chlorodimethyloctadecylsilane (CDMOS) or octadecyltrichlorosilane (OTS) with the silanol groups on the glass surface were shown to weaken the attraction of the PVP block of the block copolymer (of either the 625-49 or the 800-870 dPS-PVP) for the glass by preventing hydrogen bonding between silanol groups on the glass and the N of the PVP. Regardless of the areal chain density of the block copolymer at the interface, we find that the fracture energy is less than ~1 J/m$^2$ as shown in Fig 8 and the failure analysis with FRES and RBS shows that all the dPS and PVP are on the PS side of the fracture. Under these conditions we can show that the interface fails by pull-off without a craze being generated because the stresses that can be sustained ahead of the crack by the interface are not sufficient to cause crazing in the PS.
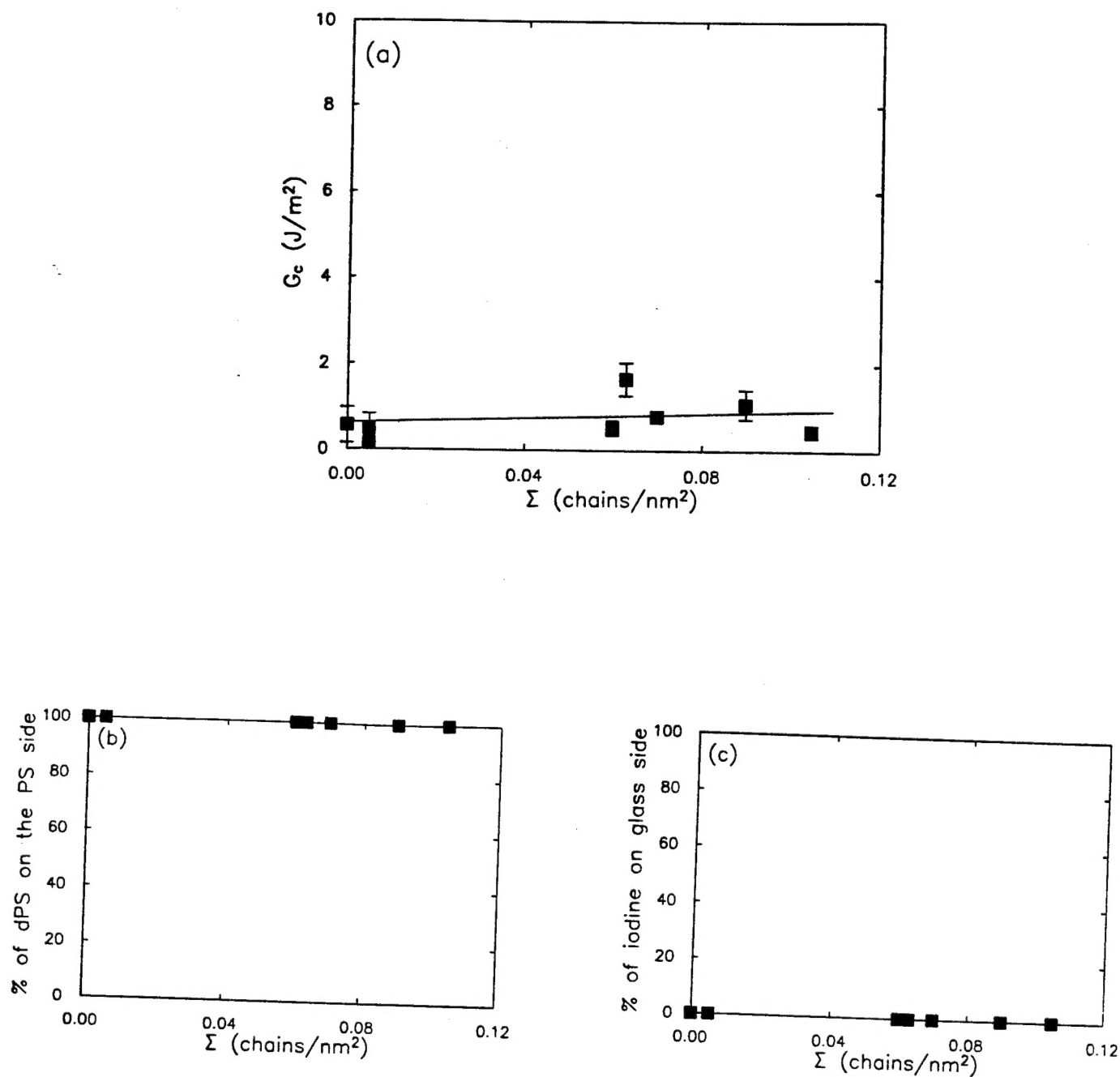
**Figure 8.** a.) Interfacial fracture energy of PS/OTS-glass interfaces modified by a 656-46 dPS-PVP block copolymer. b.) and c.) percentage of dPS on the PS and PVP (iodine)on the glass sides of the fracture surface, respectively.

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The experiments have shown that by modifying a PS-glass interface with the appropriate block copolymer or self assembled monolayer, it is possible to tailor the adhesion of the interface to be strong or weak. To provide reinforcement the block copolymer placed at an interface must have at least two blocks one of which is compatible (miscible) with the bulk homopolymer and a second anchor block which has an affinity for the glass. By weakening this affinity (as was done by covering the glass with a monolayer of CDMOS or OTS) we encourage pull-off of the anchor block and weaken the interface. Since Kramer and coworkers have shown that it is possible to form self-assembled monolayers (SAMs) with progressively less interface coverage by annealing the Si/SiO$_2$/SAM surface at progressively higher temperatures, it may be possible to provide a wide range of effective anchor block affinities by annealing the SAM layer on glass prior to bonding to the polymer.

Furthermore by choosing appropriate lengths for the blocks of the block copolymer, it is possible to dictate the failure mechanism for interfaces with strong anchor block affinities (e.g. PVP against a bare glass surface). Kramer and coworkers have demonstrated the following failure mechanisms: chain scission prior to crazing, pull-out prior to crazing as well as crazing followed by chain scission or anchor block pull-off. Each mechanism can give a certain range of failure stress, without requiring a precise control of the quantity of block copolymer at the interface. Modification of the polymer-non-polymer interface with block copolymers can be accomplished with small quantities of these block copolymers which tend to segregate there naturally. Because only small amounts of the additive are needed, control of the interface fracture toughness can be accomplished without affecting the bulk properties of either the polymer or the non-polymer layers on either side of this interface.

Publications or papers in preparation under this grant:

"The Measurement of the Fracture Toughness of Polymer-Nonpolymer Interfaces", J.W. Smith, E.J. Kramer, F. Xiao, C.-Y. Hui, W. Reichert and H.R. Brown, (MSC Report#7437), J. Materials Science, **28**, 4234-4344 (1993).

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"Tailored Adhesion at Polymer/Nonpolymer Interfaces", J.W. Smith, E.J. Kramer and P.J. Mills, (MSC Report# 7599) J. Polymer Sci.-Polymer Phys., J. Polymer Sci-Polymer Phys., **32** 1731-1744 (1994).

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"Segregation at and Fracture Toughness of Polystyrene-Silicon Oxide Interfaces", M. Calistri-Yeh, PhD Thesis, Cornell University, (1995).

"Diblock Copolymer Segregation to Silicon Oxide Interfaces", M. Calistri-Yeh, E.J.

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M. Calistri-Yeh, E.J. Kramer and R. Sharma, in preparation.